

PHENOLIC GROUP-CONTAINING PHOSPHONITE COMPOUND AND  
PROCESS FOR MAKING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

This application claims priority of Taiwanese  
5 application No. 092108102, filed on April 9, 2003.

BACKGROUND OF THE INVENTION

1. Field of the invention

This invention relates to a phosphonite compound,  
more particularly to a phenolic group-containing  
10 phosphonite compound and to the process for making  
the same.

2. Description of the related art

Stabilizers, such as primary antioxidants and  
secondary antioxidants, are used for preventing  
15 degradation of polymers when the latter is exposed  
to light or heat. Typical examples of the primary  
antioxidants are sterically hindered phenols or  
secondary aromatic amines which are capable of  
undergoing fast reactions with peroxy radicals formed  
20 in the polymers so as to terminate undesired free  
radical chain reaction in the polymers. Typical  
examples of the secondary antioxidants are sulfur  
compounds and phosphites which can react with  
hydroperoxides formed in the polymers so as to form  
25 non-radical products. It is known in the art that  
synergistic effects are observed when the primary and  
secondary oxidants are combined. However, the thermal

stability of the combinations is still poor due to low molecular weight of the aforesaid compounds. For instance, the mixture of tetrakis(methylene(3,5-di-*t*-butyl-4-hydroxyhydrocinnamate)methane (a 5 phenolic compound) and tris(2,4-di-*t*-butylphenyl)phosphite (a phosphite compound) blended in a ratio of 1:4, which can obtain good anti-oxidation effect, is poor in thermal stability due to the tendency of decomposition of the aforesaid 10 phosphite compound at elevated temperatures. The phosphite compound completely decomposes at a temperature of about 350°C.

U.S. Patent Nos. 4,185,006, 4,276,232, 4,380,515, and 4,661,440 disclose phosphonite 15 stabilizers that have larger molecular weight than those of the aforesaid phenolic compounds and phosphites, which renders the phosphonite stabilizers to have better thermal stability than those of the aforesaid phenolic compounds and 20 phosphites. The disclosures of the aforesaid U.S. Patents are incorporated herein by reference.

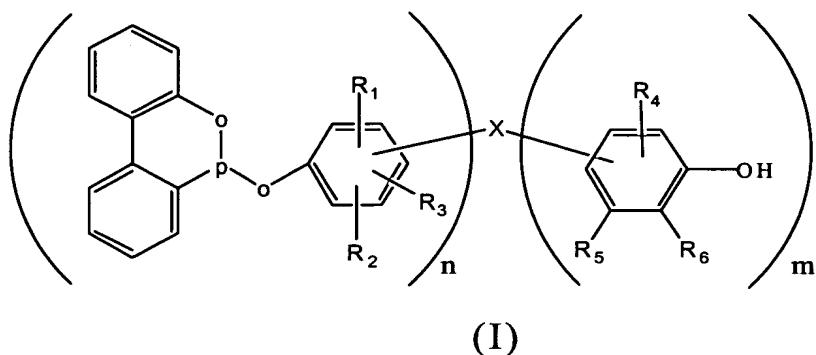
#### SUMMARY OF THE INVENTION

The object of the present invention is to provide a phenolic group-containing phosphonite compound 25 that not only combines the functions of the aforesaid phenolic compounds and phosphites, but also possesses better thermal stability over the aforesaid phenolic

compounds and phosphites.

According to one aspect of the present invention, there is provided a phenolic group-containing phosphonite compound of formula (I)

5



wherein

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, and R<sub>6</sub> independently of one another  
10 are hydrogen or C<sub>1</sub>-C<sub>18</sub> alkyl,

n and m are integer numbers ranging from 1 to 3, and  
the sum of n and m ranges from 2 to 4, and

wherein

X, if the sum of n and m is 2, is sulfur or C<sub>1</sub>-C<sub>8</sub>  
15 alkylene which may be optionally substituted with at  
least one C<sub>1</sub>-C<sub>6</sub> alkyl,

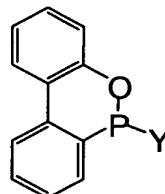
X, if the sum of n and m is 3, is a trivalent moiety  
of C<sub>3</sub>-C<sub>7</sub> aliphatic group, and

X, if the sum of n and m is 4, is a tetravalent moiety  
20 of C<sub>4</sub>-C<sub>10</sub> aliphatic group.

According to another aspect of the present

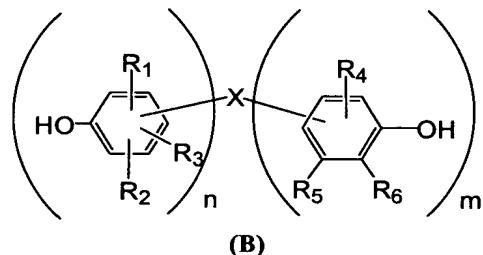
invention, there is provided a polymer composition that comprises a polymer material and the compound of formula (I).

According to yet another aspect of the present invention, there is provided a process for preparing the compound of formula (I). The process comprises the step of reacting a phosphonite compound of formula (A)



(A)

wherein Y is halogen, with a phenolic compound of formula (B)



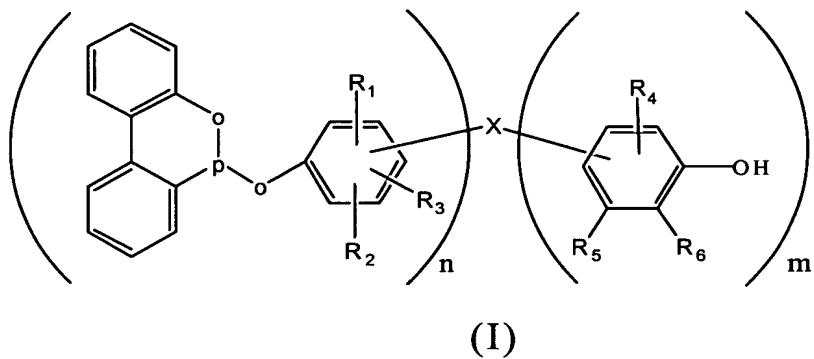
wherein n, m, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, and X have the same meanings as defined in the forgoing, in a non-acidic reaction condition.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

This invention provides a phenolic group-containing phosphonite compound that can serve as a

stabilizer for polymers, that combines the functions of the aforesaid phenolic compounds and phosphites, which are capable of reacting with peroxy radicals and hydroperoxides, respectively, and that possesses 5 better thermal stability over the aforesaid phenolic compounds and phosphites.

The phenolic group-containing phosphonite compound has the following formula (I)



10

wherein

$R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ , and  $R_6$  independently of one another are hydrogen or  $C_1-C_{18}$  alkyl,

15  $n$  and  $m$  are integer numbers ranging from 1 to 3, and the sum of  $n$  and  $m$  ranges from 2 to 4, and

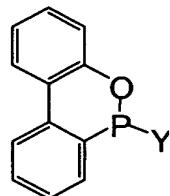
wherein

$X$ , if the sum of  $n$  and  $m$  is 2, is sulfur or  $C_1-C_8$  alkylene which may be optionally substituted with at least one  $C_1-C_6$  alkyl,

20  $X$ , if the sum of  $n$  and  $m$  is 3, is a trivalent moiety of  $C_3-C_7$  aliphatic group, and

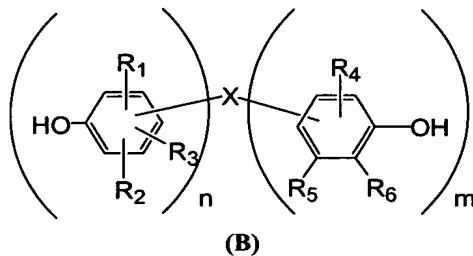
X, if the sum of n and m is 4, is a tetravalent moiety of C<sub>4</sub>-C<sub>10</sub> aliphatic group.

The phenolic group-containing phosphonite compound of formula (I) can be prepared through 5 esterification or transesterification reactions, for example, by reacting a phosphonite compound of formula (A)



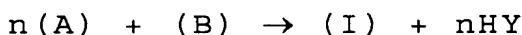
(A)

10 wherein Y is halogen, with a phenolic compound of formula (B)



(B)

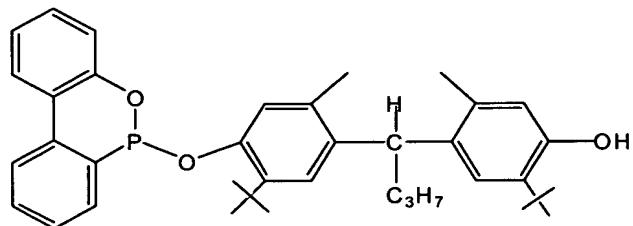
wherein n, m, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>, R<sub>5</sub>, R<sub>6</sub>, and X have the same meanings as defined in the forgoing, in a 15 non-acidic reaction condition. The aforesaid reaction can be represented as follows



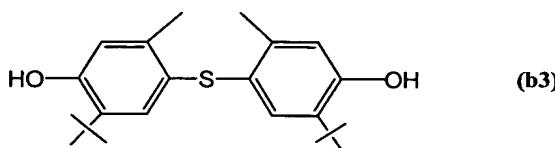
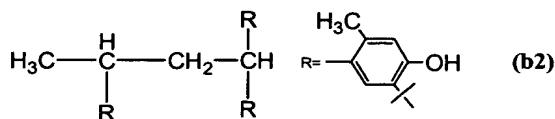
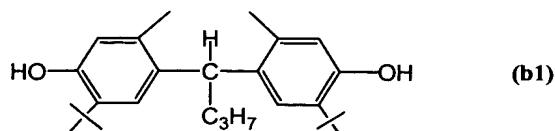
Preferably, the reaction is carried out in the presence of a base in an inert solvent. The base is

preferably selected from the group consisting of amine, triethylamine, pyridine, N,N'-dimethylaniline, sodium carbonate, and the mixtures thereof. The inert solvent is preferably an aprotic solvent, such as petroleum ether, toluene, xylene, methyl-ethyl ketone, acetonitrile, and ethyl acetate. 5 Amine can also be used as solvent.

In a preferred embodiment, the phenolic group-containing phosphonite compound of formula (I) 10 is 6-(4,4'-butylidene-2-t-butyl-5-methylphenol-2'-t-butyl-5'-methylphenoxy)dibenz[c,e]-[1,2]oxaphosphorine, i.e., n and m are 1, X is propylmethylene, R<sub>1</sub> and R<sub>4</sub> are methyl, R<sub>2</sub> and R<sub>6</sub> are t-butyl, and R<sub>3</sub> and R<sub>5</sub> are hydrogen. The structure of 15 the preferred embodiment is as follows



The phenolic compound of formula (B) for preparing 6-(4,4'-butylidene-2-t-butyl-5-20 methylphenol-2'-t-butyl-5'-methylphenoxy)dibenz[c,e]-[1,2]oxaphosphorine can be one of the following compounds (b1), (b2), (b3).



The thus formed compound 6-(4,4'-butylidene-2-t-butyl-5-methylphenol-2'-t-butyl-5'-methylphenoxy)dibenz[c,e]-[1,2]oxaphosphorine shows excellent thermal stability. In a thermal test with an increase in temperature, the compound is only partially decomposed (up to 48% is not decomposed) when the temperature reaches about 400 °C (the aforesaid phenolic compounds and phosphites are completely decomposed under this temperature).

The present invention is also related to a polymer composition that comprises a polymer material and the phenolic group-containing phosphonite compound of formula (I). The polymer material may be polyolefins (for example polyethylene and polypropylene) and its copolymers, polystyrene and its copolymers (such as acrylonitrile-butadiene-styrene), polyamide, linear polyester, polyurethane, polycarbonate, elastomer, and polyvinyl chloride.

The phenolic group-containing phosphonite compound of formula (I) is preferably in an amount of from 0.005 to 5wt% of the polymer composition, and more preferably from 0.05 to 0.5wt% of the polymer composition.

#### Examples and Comparative Examples

The present invention will be described in more detail in the following Examples.

10

##### A. Preparation of 6-(4,4'-butylidene-2-t-butyl-5-methylphenol-2'-t-butyl-5'-methylphenoxy)dibenz[c,e]-[1,2]oxaphosphorine

46.95g (0.2mole) of 6-chloro-15 dibenz[c,e][1,2]oxaphosphorine, 84.26g of 4,4'-butylidenebis(2-t-butyl-5-methylphenol), 120ml triethylamine and 350ml toluene were added into a reactor. Reaction was carried out at a temperature of about 80°C for 18 hours. After the reaction, the 20 reaction mixture was subjected to filtration and crystallization to obtain a crystalline product that has a melting point 75±5°C.

##### B. Materials For Preparation of Stabilizers

25 (a) : 6-(4,4'-butylidene-2-t-butyl-5-methylphenol-2'-t-butyl-5'-methylphenoxy)dibenz[c,e]-[1,2]oxaphosphorine

(b) : tetrakis(methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)methane

(c) : octadecyl 3-(3',5'-di-t-butyl-4'-hydroxy-phenyl)propionate

5 (d) : tris(2,4-di-t-butylphenyl)phosphite

(e) : cyclic neopentanetetrayl bis(octadecyl phosphite)

C. Stabilizers (Examples 1-7 and Comparative Examples 1-3)

The stabilizers shown in Table 1 were prepared  
10 using different combinations of the materials listed  
above.

Table 1

| Example             | Material        | Weight Ratio |
|---------------------|-----------------|--------------|
| 1                   | (a)             | -            |
| 2                   | (a) / (d)       | 1:1          |
| 3                   | (a) / (b)       | 1:1          |
| 4                   | (a) / (d) / (b) | 1:1          |
| 5                   | (a) / (e)       | 1:1          |
| 6                   | (a) / (c)       | 2:1:1        |
| 7                   | (a) / (c) / (e) | 2:1:1        |
| Comparative Example | Material        | Ratio        |
| 1                   | (c) / (d)       | 1:4          |
| 2                   | (b) / (d)       | 1:2          |
| 3                   | (c) / (e)       | 1:2          |

15 D. Polymer Compositions (Examples 8-23 and Comparative Examples 4-10)

The polymer compositions shown in Table 2 are  
combinations of polypropylene (PP) and the  
stabilizers shown in Table 1. Each polymer  
20 composition was prepared by blending the stabilizer

and the polymer in a single screw extruder under a temperature of less than 230 °C . A small amount (1200ppm) of additive (calcium sterate) was added into each polymer composition.

5

Table 2 (PP Polymer)

| Example             | stabilizer            | Amount of stabilizer, ppm |
|---------------------|-----------------------|---------------------------|
| 8                   | Example 1             | 500                       |
| 9                   | Example 1             | 1000                      |
| 10                  | Example 1             | 2000                      |
| 11                  | Example 2             | 1000                      |
| 12                  | Example 3             | 1000                      |
| 13                  | Example 4             | 1000                      |
| Comparative Example | stabilizer            | mount of stabilizer, ppm  |
| 4                   | Comparative Example 2 | 500                       |
| 5                   | Comparative Example 2 | 1000                      |

10 The polymer compositions shown in Table 3 are combinations of polyethylene (PE) and the stabilizers shown in Table 1. Each polymer composition was prepared by blending the stabilizer and the polymer in the single screw extruder under a temperature of less than 200°C . A small amount (1200ppm) of additive (calcium sterate) was added into each polymer composition.

15

Table 3 (PE Polymer)

| Example             | stabilizer            | Amount of stabilizer, ppm |
|---------------------|-----------------------|---------------------------|
| 14                  | Example 1             | 500                       |
| 15                  | Example 1             | 1000                      |
| 16                  | Example 1             | 2000                      |
| 17                  | Example 2             | 1000                      |
| 18                  | Example 3             | 1000                      |
| 19                  | Example 4             | 1000                      |
| Comparative Example | stabilizer            | mount of stabilizer, ppm  |
| 6                   | Comparative Example 1 | 500                       |
| 7                   | Comparative Example 1 | 1000                      |
| 8                   | Comparative Example 2 | 500                       |
| 9                   | Comparative Example 2 | 1000                      |

The polymer compositions shown in Table 4 are combinations of acrylonitrile-butadiene-styrene (ABS) and the stabilizers shown in Table 1. Each polymer composition was prepared by blending the 5 stabilizer and the polymer in the single screw extruder under a temperature of about 220°C.

Table 4 (ABS Polymer)

| Example             | stabilizer            | Amount of stabilizer, ppm |
|---------------------|-----------------------|---------------------------|
| 20                  | Example 1             | 1000                      |
| 21                  | Example 5             | 1000                      |
| 22                  | Example 6             | 1000                      |
| 23                  | Example 7             | 1000                      |
| Comparative Example | stabilizer            | Amount of stabilizer, ppm |
| 10                  | Comparative Example 3 | 100                       |

10 E. Results

Each polymer composition shown in Tables 2 and 3 was measured for yellowing (b=+yellow/-blue, higher b value means more severe yellowing), and Melt index (MI) (higher MI value means more severe material degradation). The results are respectively shown in Tables 5 and 6 for polymer PP and Tables 7 and 8 for polymer PE. A spectrophotometer was used for measuring the yellowing and Yellowness Index of the polymer compositions.

Table 5 (PP polymer)

| Example             | b value, prior to extrusion | b value, after  |                 |                 |
|---------------------|-----------------------------|-----------------|-----------------|-----------------|
|                     |                             | first extrusion | third extrusion | fifth extrusion |
| blank               | -0.75                       | -0.11           | 1.22            | 2.54            |
| 8                   | -1.82                       | -1.68           | -1.05           | -0.91           |
| 9                   | -1.85                       | -1.72           | -1.34           | -1.07           |
| 10                  | -1.90                       | -1.82           | -1.68           | -1.52           |
| 11                  | -1.80                       | -1.70           | -1.08           | -0.92           |
| 12                  | -1.78                       | -1.70           | -1.12           | -0.95           |
| 13                  | -1.80                       | -1.71           | -1.15           | -0.97           |
| Comparative Example | b value, prior to extrusion | first extrusion | third extrusion | fifth extrusion |
| 2                   | -1.52                       | -1.02           | -0.31           | 0.25            |
| 2                   | -1.60                       | -1.19           | -0.76           | -0.27           |

Table 6 (PP polymer)

| Example             | MI value, prior to extrusion | MI value, after |                 |                 |
|---------------------|------------------------------|-----------------|-----------------|-----------------|
|                     |                              | first extrusion | third extrusion | fifth extrusion |
| blank               | 4.5                          | 5.1             | 6.2             | 8.3             |
| 8                   | 3.2                          | 3.3             | 3.6             | 4.0             |
| 9                   | 3.0                          | 3.1             | 3.2             | 3.4             |
| 10                  | 3.0                          | 3.1             | 3.1             | 3.2             |
| 11                  | 3.1                          | 3.2             | 3.4             | 3.8             |
| 12                  | 3.1                          | 3.2             | 3.4             | 3.7             |
| 13                  | 3.0                          | 3.2             | 3.5             | 3.7             |
| Comparative Example | b value, prior to extrusion  | first extrusion | third extrusion | fifth extrusion |
| 2                   | 4.2                          | 4.8             | 5.8             | 6.5             |
| 2                   | 4.2                          | 4.6             | 5.3             | 5.6             |

5

Table 7 (PE polymer)

| Example             | b value, prior to extrusion | b value, after  |                 |                 |
|---------------------|-----------------------------|-----------------|-----------------|-----------------|
|                     |                             | first extrusion | third extrusion | fifth extrusion |
| blank               | -0.85                       | 1.05            | 3.85            | 4.2             |
| 14                  | -2.32                       | -2.25           | -1.66           | -1.0.87         |
| 15                  | -2.13                       | -2.21           | -1.86           | -1.07           |
| 16                  | -2.25                       | -2.22           | -2.02           | -1.68           |
| 17                  | -2.26                       | -2.21           | -1.75           | -1.00           |
| 18                  | -2.18                       | -2.20           | -1.76           | -1.02           |
| 19                  | -2.24                       | -2.21           | -1.8            | -1.05           |
| Comparative Example | b value, prior to extrusion | first extrusion | third extrusion | fifth extrusion |
| 6                   | -1.29                       | -1.03           | -0.4            | -0.2            |
| 7                   | -1.51                       | -0.87           | 0.77            | 1.66            |
| 8                   | -1.81                       | -1.69           | -0.96           | -0.78           |
| 9                   | -2.48                       | -2.12           | -1.02           | -0.02           |

Table 8 (PE polymer)

| Example             | MI value, prior to extrusion | MI value, after |                 |                 |
|---------------------|------------------------------|-----------------|-----------------|-----------------|
|                     |                              | first extrusion | third extrusion | fifth extrusion |
| blank               | 0.25                         | 0.19            | 0.12            | 0.10            |
| 14                  | 0.25                         | 0.25            | 0.23            | 0.21            |
| 15                  | 0.25                         | 0.26            | 0.26            | 0.25            |
| 16                  | 0.25                         | 0.26            | 0.25            | 0.25            |
| 17                  | 0.25                         | 0.25            | 0.24            | 0.23            |
| 18                  | 0.25                         | 0.25            | 0.25            | 0.26            |
| 19                  | 0.25                         | 0.25            | 0.24            | 0.25            |
| Comparative Example | b value, prior to extrusion  | first extrusion | third extrusion | fifth extrusion |
| 6                   | 0.25                         | 0.20            | 0.15            | 0.14            |
| 7                   | 0.25                         | 0.25            | 0.23            | 0.21            |
| 8                   | 0.25                         | 0.21            | 0.18            | 0.16            |
| 9                   | 0.25                         | 0.25            | 0.23            | 0.20            |

Each polymer composition shown in Table 4 was measured for Yellowness Index (YI) (higher YI value means more severe yellowing) prior to and after curing in an oven under a temperature of 180°C for 2 hours. The difference (Δ YI) between initial YI and YI after curing was calculated. The results are shown in Table 9.

10

Table 9 (ABS)

| Example             | YI value after extrusion |                 |      |
|---------------------|--------------------------|-----------------|------|
|                     | Initial YI               | YI after curing | Δ YI |
| blank               | 14                       | 75              | 61   |
| 20                  | 11                       | 52              | 41   |
| 21                  | 12                       | 57              | 45   |
| 22                  | 12                       | 58              | 46   |
| 23                  | 11                       | 55              | 44   |
| Comparative Example | Initial YI               | YI after curing | Δ YI |
| 10                  | 12                       | 60              | 48   |

The results (Tables 5 to 9) show that the phenolic group-containing phosphonite compound of formula (I) combines the functions of the aforesaid

phenolic compounds and phosphites, and possesses better thermal stability over the aforesaid phenolic compounds and phosphites.

With the invention thus explained, it is  
5 apparent that various modifications and variations  
can be made without departing from the spirit of the  
present invention.